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On the model describing potentiostatic current transients recorded during the mass transport-controlled nucleation of hemispheres in the presence of forced convection

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Abstract

In this work it is shown from analysis of experimental current density transients, recorded during copper electrodeposition, under force convection condition, that the use of the so called current density correction, j_0, proposed for Hyde et al. (M. E. Hyde, O.V. Klymenko, R.G. Compton, The theory of electrodeposition in the presence of forced convection: Transport controlled nucleation of hemispheres, J. Electroanal. Chem. 534 (2002) 13) for fitting purposes only is not recommended, since it provokes that the related values with physical meaning, for instance the diffusion layer thickness (δ) shifts away from the correct values, found using the equation proposed by Levich (B. Levich, Physicochemical Hydrodynamics, Prentice, (1962)).

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Nomenclature

t	time
j	current density
D	diffusion coefficient
c	concentration
M	molar mass
ρ	density of the depositing species
F	Faraday constant
z	number of electron transfered
v	potential scan rate
N_0	Number density of actives sites
A	nucleation rate constant
η	overpotential
T	temperature
R	gas constant
ω	angular speed
δ	diffusion layer thickness
θ_{ex}	overall coverage
δ	diffusion layer thickness
δ_{lim}	limiting value of the thickness of the diffusion layer
j_0	current density correction

1. Introduction

The fundamental understanding of the electrodeposition process of metals has been the subject of increasing interest, because it is specifically relevant to obtain materials having specific properties and dimensions, particularly when addressing economically-driving aspects as electrocatalytic activity, more so in the context of the synthesis and application of nanoparticles. In this particular sense, one of the basic aspects involved during formation of new phases is the clear possibility to exert direct influence and relatively close control on supersaturation, through application of diverse overpotential conditions during formation of metal phases. Electrochemical methods possess unique capabilities to study, modify surfaces with a sense of design and with significant rate-controlling possibilities of the overall process, as well as to exert direct influence on the resulting morphologies and dimensionality.

Furthermore, there are theoretical models capable of describing adequately the chronoamperometric response of 3D diffusion-limited multiple nucleation metal systems like those having a diffusion layer thickness, δ, which varies with time[1-4]. In this same respect, when the system is subjected to forced convection conditions, as imposed either through ultrasound, cell agitation or a rotating disc electrode, RDE, the electrochemical nucleation and growth processes of new phases under these conditions have received less attention[5]. However, there is no theoretical model capable of describing the experimental current transients within the full range of variation of the angular speed, ω, even before the thickness of the diffusion layer reaches its limiting value δ_{lim}.The following considerations will be on the model published by Hyde et al.[5], which describes the potentiostatic current transients under forced convection conditions, as imposed in their work by means of ultrasound. When there is time-independent formation of N nuclei, then the extended overall coverage, θ_{ex}, is given by (1):

$$\theta_{ex} = \int_0^t \frac{dN}{du}(u) S(t - {}_i u) du \tag{1}$$

where $(t - {}_i u) = {}_i \tau$. By using $dN / du = iAN_0 e^{-Au}$ then,

$$\theta_{ex}=\left(2\sqrt{2}\pi\left(\frac{Mc}{\rho}\right)^{1/2}\left[1-\exp\left(\frac{-zF}{RT}\eta\right)\right]^{1/2}D^{1/2}\delta AN_0\right)\int_0^t(t-u)^{1/2}e^{-Au}du \tag{2}$$

In order to calculate the overall current density, the following is required: $j=zF\left(Dc/\delta\right)$, combined with Avrami's theorem[1]:

$$j=zF\frac{Dc}{\delta}\theta=zF\frac{Dc}{\delta}\left(1-e^{-\theta_{ex}}\right) \tag{3}$$

This gives:

$$j=zF\frac{Dc}{\delta}\left[1-\exp\left(-BA\int_0^t(t-u)^{1/2}e^{-Au}du\right)\right] \tag{4}$$

Where $B=\left(2\sqrt{2}\pi\left(\frac{Mc}{\rho}\right)^{1/2}\left[1-\exp\left(\frac{-zF}{RT}\eta\right)\right]^{1/2}D^{1/2}\delta AN_0\right)$. To evaluate the integrals in equations (2) and (4), the substitution $x={}^{i(t-u)}\!/_{t}$ is done, so that:

$$\int_0^t(t-u)^{1/2}e^{-Au}du=t^{3/2}e^{-At}\int_0^1x^{1/2}e^{Atx}dx=t^{3/2}e^{-At}\left(\frac{e^{At}}{At}-\frac{1}{i(At)^{3/2}}\int_0^{i(At)^{1/2}}e^{-x^2}dx\right)=\frac{t^{1/2}}{A}-\frac{\pi^{1/2}}{2}A^{-3/2}e^{-At}erfi\left[(At)^{1/2}\right] \tag{5}$$

Where $erfi(z)={}^{erf(iz)}\!/_{i}$, is the imaginary error function.

$$erfi(z)=2\pi^{-(1/2)}\sum_{n=0}^{\infty}\frac{z^{2n+1}}{n!(2n+1)} \tag{6}$$

Thus, this integral is given by:

$$\int_0^t(t-u)^{1/2}e^{-Au}du=\frac{t^{1/2}}{A}-A^{-3/2}e^{-At}\sum_{n=0}^{\infty}\frac{(At)^{(n+(1/2))}}{n!(2n+1)}=\frac{t^{1/2}}{A}\left(1-e^{-At}\sum_{n=0}^{\infty}\frac{(At)^n}{n!(2n+1)}\right) \tag{7}$$

Alternatively, the solution of the integral in equation (7) can be written using the confluent hypergeometric function[10]:

$$\frac{2}{3}{}_1F_1\left(1,\frac{5}{2},-At\right) \tag{8}$$

Combining equations (4) and (7) one obtains:

$$j=zF\frac{Dc}{\delta}\left[1-\exp\left\{-B\sqrt{t}\left(1-e^{-At}\sum_{n=0}^{\infty}\frac{(At)^n}{n!(2n+1)}\right)\right\}\right] \tag{9}$$

This result implies that the current density response should depict a transient that increases monotonically with the limiting current density, for one species, that only depends on the external agitation force. The analysis of the curves was accomplished with the aid of a modification done to Scharifker and Mostany's equation[1], which is written again considering only the relevant part of the current density response:

$$j = \left\{ \sqrt{2} zFc\pi D^{3/2} \left(\frac{Mc}{\delta} \right)^{1/2} \left[1 - \exp\left(\frac{-zF}{RT} \eta \right) \right]^{1/2} N_0 A \right\} t^{3/2} \tag{10}$$

Compton and coworkers introduced, for the sake of their fitting procedure, an induction time, t_0, and a correction for the current density, j_0:

$$j = j_0 + k\left(t - t_0\right)^{3/2} \tag{11}$$

Where, k is the term found in equation (10):

$$k = \sqrt{2} zFc\pi D^{3/2} \left(\frac{Mc}{\delta} \right)^{1/2} \left[1 - \exp\left(\frac{-zF}{RT} \eta \right) \right]^{1/2} N_0 A \tag{12}$$

In order to examine the validity of the expressions and the applicability of the model, experimental data were compared considering constant the thickness of the diffusion layer, the response of the potentiostatic current density of a 3D nucleation and growth process, with an approximation of equation (9), as follows[5]:

$$j = zF \frac{cD}{\delta} \left[1 - \exp\left(-\left(2\sqrt{2\pi} \left(\frac{Mc}{\rho} \right)^{1/2} \left[1 - \exp\left(\left(-\frac{zF}{RT} \right) \eta \right) \right] D^{1/2} N_0 \delta \right) t^{1/2} \right) \right] \left\{ 1 - e^{-At} \left[1 + \frac{At}{3} + \frac{(At)^2}{10} + \frac{(At)^3}{42} + \ldots \right] \right\} + j_0 \tag{13}$$

2. Experimental conditions

The deposition of copper onto glassy carbon, GC, was carried out in a conventional three-electrode cell with an aqueous solution of 5 mM $Cu(NO_3)_2$ with KCl 0.1 mM and 0.73 M H_2SO_4, from analytical grade substances, from Aldrich y Mallinckrodt, using deionised water Type I, with a resistivity of 17.6 MΩcm, from a Millipore-Q equipment. Nitrogen was bubbled through nitrogen for at least 15 min to remove dissolved oxygen. The working electrode, WE, was built with a glassy carbon disc and a platinum ring, with a surface area of 0.1662 and 1.81 x 10^{-3} cm^2, respectively. The counter electrode, CE, was also platinum having an area which was larger than that of ring of the working electrode. The reference electrode was a SCE, to which successively all potentials cited in this work should be referred.

An Autolab 30 potentiostat-galvanostat permitted to establish the potential applied to the working electrode; as customary, this set up was connected to a PC to facilitate control of the experiments and to acquire data by means of the GPES data processing software. The rate of rotation of the WE by means of the DC motor of the Pine Instruments Company, MSRX Speed Control, Analytical Rotator, Model AFMSRX, Serial 1018. The angular speed was controlled within the 0 – 3000 rpm interval.

3. Results and discussions

3.1. Analysis of the potentiostatic current density transients

3.1.1. Using j_0

Figure 1 shows a family of experimental potentiostatic current density transients obtained during copper electrodeposition onto glassy carbon, as a function the angular speed of the RDE and a constant applied potential. It is possible to note that for $\omega > 500$ rpm the potentiostatic current density transients depicts the characteristic features describe by Hyde et al.[1] thus they will be analysed with this model, see below.

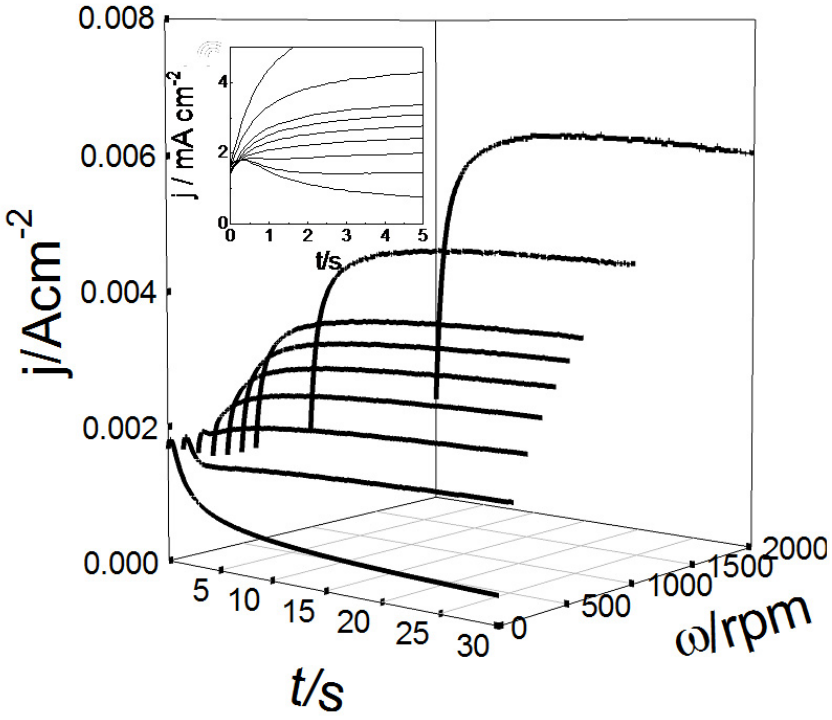

Fig. 1. (a) Family of experimental potentiostatic current density transients recorded during copper electrodeposition in the system GC / 5 mM Cu $(NO_3)_2$, 0.1 M KCl, for a constant potential of -0.27 V and different working electrode rotation speeds.

Hyde et al.[1] have derived, so far, the only model, see equation (13) for the potentiostatic nucleation and three dimensional growth of deposits on an electrode surface under hydrodynamic conditions. Figure 2b show the comparison of an experimental current transient and the corresponding theoretical one generated by no-linear fitting of eqn. (13) to the experimental data. It is possible no note that Hyde et al. model provides excellent fitting to the experimental data recorded at a high electrode rotation speed. From this analysis it is possible to estimate the value of the diffusion layer, δ, see Figure 3. Moreover, δ values can be independently obtained using the Levich equation[6] (14). Figure 3 show the comparison of the δ values calculated from eqns. (13) and (14) and it is plaint that they are different, particularly for the lowest electrode rotation speeds.

$$\delta = D^{1/3} \nu^{-1/6} \omega^{-1/2} \tag{14}$$

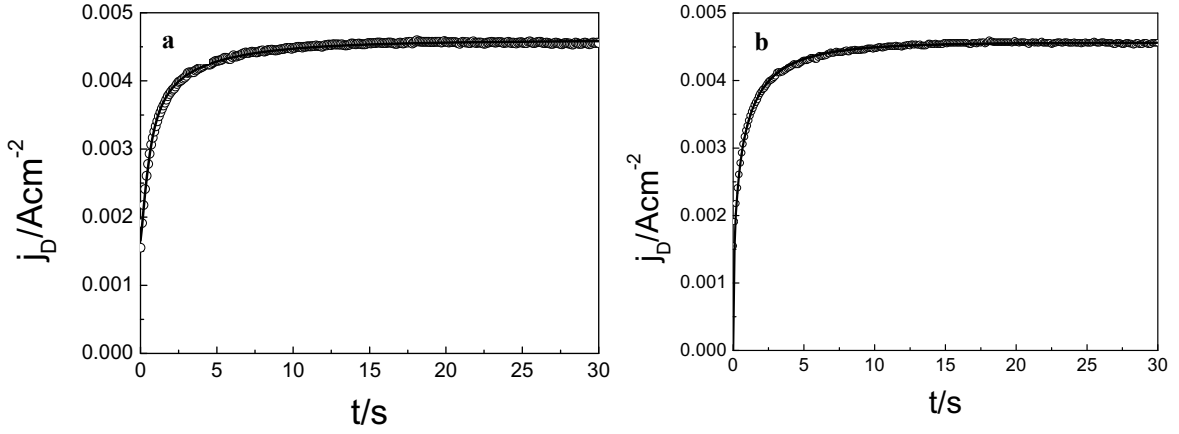

Fig. 2. Comparison of and experimental (OOO) potentiostatic current density transient recorded during copper electrodeposition at -0.27 V and 600 rpms, see Figure 1, with the theoretical one (---) generated from the non-linear fit of eqn. (13) a) with and b) without j_0.

3.1.2. Without using j_0

In spite that equation (13) provides excellent fittings to the experimental data recorded at high electrode rotation speeds, it includes a term j_0 that was proposed for fitting purposes only. So far we have shown from analysis of experimental data recorded during copper electrodeposition under force convection condition, that the use of j_0 is not recommended, since it provokes that the related values with physical meaning, for instance the diffusion layer thickness (δ) see Figure 3, shifts away from the correct values, found using equation (14) proposed by Levich[6]. Figure 2b show the comparison of an experimental current transient and the corresponding theoretical one generated by no-linear fitting of eqn. (13) without j_0 to the experimental data. The δ values calculated from eqn. (13) without j_0 are also plotted in Figure 3 and it is possible to note that these values are much closer to those calculate using eqn. (14) for all the electrode rotation speeds considered.

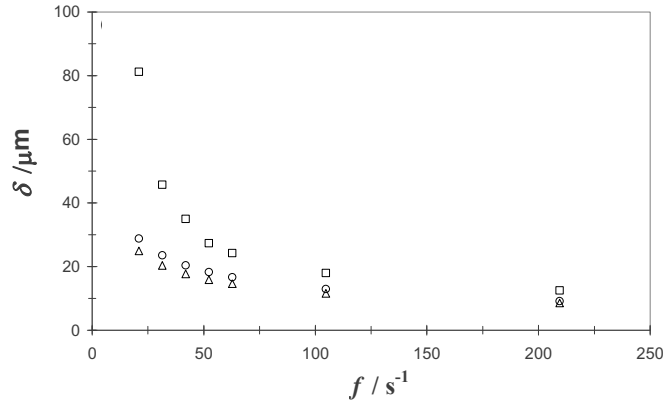

Fig. 3. Comparison of the values of diffusion layer δ obtained from different approaches, namely: analysis of potentiostatic current density transient, see Figure 1, using equation (13) with j_0 (□), without j_0 (O) and (Δ) determined from Levich equation (14).

4. Conclusions

The use of current density correction, j_0, in eqn. (13) does not show a significant contribution for the analysis of experimental current density. In the case of copper electrodeposition when eqn. (13) includes j_0, the value estimated for the thickness of the diffusion, δ, layer away from the behavior predicted by Levich, however when j_0 was not

included the δ values were much closer to those calculate using the Levich equation (14) for all the electrode rotation speeds considered.

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